

# Photoelectrochemical Splitting of Water: Using Porphyrins as Catalysts

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## **Abstract**

Photoelectrochemical Water Splitting: Using Porphyrins as Catalysts. Scott Warren (Whitman College, Walla Walla, Washington, 99362). A. Bansal (National Renewable Energy Laboratory, Golden, Colorado 80401).

Bandedge engineering was performed on GaInP<sub>2</sub> semiconductor so that the conduction and valence bands would overlap the water redox potentials, with the goal of creating a monolithic water-splitting device. Porphyrins were applied to the surface of the GaInP<sub>2</sub> primarily by drop-evaporation methods. Mott-Schottky analyses in pH 4 and pH 7 buffers showed that Cobalt Tetraphenyl Porphyrin (CoTPP) was the most successful bandedge-shifting molecule. In pH 4, CoTPP shifted band edges in the positive direction by 400mV, so that overlap of the water redox potentials occurred. A study in light showed that CoTPP did not catalyze charge transfer. Further attempts will be made at finding a porphyrin that can shift the bandedge position and catalyze charge transfer.

### **Research Category:**

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## **Introduction**

In recent years, there has been an increase in the research of renewable energy as the limitations of traditional forms of energy have become apparent. The United States' dependence on fossil fuels is both a major pollution hazard and a future national security issue as foreign oil supplies run low. Developing a renewable energy resource that does not pollute will solve both of these problems. Hydrogen is among the most promising replacements for fossil fuels.

Hydrogen eliminates fossil fuels' shortcomings. When hydrogen is combined with air in a fuel cell, the only product is water—there is absolutely no pollution. Additionally, hydrogen can be readily produced from a variety of sources. One common method includes passing a large quantity of electricity through water to split it into hydrogen and oxygen gas. However, the electricity needed to split the water must come from somewhere—perhaps a coal plant, which detracts from hydrogen's non-polluting benefits. Also, the large amount of electricity needed makes the hydrogen expensive to produce and unable to compete with cheaper fuels. Consequently, finding a method to produce hydrogen cheaply and efficiently from a renewable source is the first step in developing a safe and non-polluting energy resource.

Our group's research aims to develop an economically viable water-splitting system to produce hydrogen. Similar to the above-mentioned system, we use electricity to split water into hydrogen and oxygen. However, our electricity is generated from solar cells immersed in the water. The electricity enters the water directly from the solar cell, producing hydrogen right on the surface of the solar panel. The hydrogen is collected and stored in tanks for use in a variety of applications. This system for hydrogen production is more efficient and requires less energy than others, so it enables the hydrogen to compete economically with other forms of energy.

The purpose of our research is to overcome two problems related to our water-splitting system. The first problem is to make the system energetically favorable—that is, to split as much hydrogen with as little energy input from the solar cell as possible. The key is to get the energy level at the surface of the solar cell (a semiconductor made of gallium indium phosphide) to exactly match the energy level needed to split the water into hydrogen and oxygen. Modification of the semiconductor's energy level occurs by applying organic molecules to the semiconductor's surface. Research by members of our group has suggested that organic molecules with a large dipole moment are good candidates for shifting the energy level to an optimal position (Kocha, 1995).

The second problem relates to making the semiconductor stable in water. When the transfer of electricity from the solar cell to the water is too slow, the surface becomes unstable. The surface corrodes, making the system less energetically favorable. Research has shown that this problem can be corrected by applying transition-metal ions to the surface of the semiconductor (Bansal et al., 2000; Allongue et al., 1984; Kobayashi et al., 1994). This allows the electricity to transfer quickly from the semiconductor to the water and prevent surface corrosion. By applying a metal porphyrin to the surface of the semiconductor, we hope to show how the water-splitting system has become energetically favorable and the surface of the semiconductor has become stable in water through catalysis of the electron transfer.

We hope that our work will lead to an economically viable system that will provide hydrogen through a cheap, efficient, and pollution-free method. With our most recent research, our goal is closer to becoming a reality.

## Experimental Section

Semiconductor samples were grown at NREL using organometallic chemical vapor deposition on gallium arsenide (GaAs) substrates. The carrier concentrations of the layers ranged from  $1 \times 10^{16}$  to  $1 \times 10^{18}$ . The extra p-layer of GaInP<sub>2</sub> was grown to a thickness of 0.1mm with a doping density of about  $1 \times 10^{18}$ . The modified GaInP<sub>2</sub>/GaAs samples were cut into individual unit cells using a diamond scribe. The back surface of the cell was a gold film ohmic contact, and an insulated wire was attached to the back of the device using electrically conductive silver epoxy (H-31, Epoxy Technology Inc.). After curing the epoxy in an oven at 80°C for a few hours the backside and edges of the electrode were sealed with a non-conducting epoxy (Hysol 9462, Dexter Corp.) so that the GaInP<sub>2</sub> semiconductor was the only exposed surface of the electrode.

Porphyrins were manufactured by Midcentury. The porphyrins included in the analysis were iron tetraphenyl porphyrin chloride (FeTPPCL), cobalt tetraphenyl porphyrin (CoTPP), tetrapyrrolyl porphyrin (TpyP), tetramethylpyrrolyl porphyrin chloride (TMpyPCL), sodium tetrapyrrolyl porphyrin (NaTpyP), sodium tetrasulfonatophenyl porphyrin (NaTSPP). Dichloroethane (DCE) was used to make 0.1mM solutions of FeTPPCL, CoTPP, and TpyP. Potassium sulfate (K<sub>2</sub>SO<sub>4</sub>) of 0.2M concentration with a pH of -0.1 was used to make 0.1mM solutions of TMpyPCL and NaTpyP. A pH 7 phosphate buffer was used to make 0.1mM solutions of TMpyPCL and NaTSPP.

The electrodes were etched in concentrated sulfuric acid for 10 seconds, concentrated ammonium sulfide for 15 minutes, or a hydrochloric acid:acetic acid:hydrogen peroxide 1:20:1 solution for 15 seconds. Because no significant difference was measured between the various etches, concentrated sulfuric acid was used for the majority of the experiments. The electrodes

were rinsed in water, and dried in a stream of nitrogen gas. After drying, the porphyrin solutions were applied to the semiconductor by drop-evaporation or by performing the experiment in the porphyrin solution.

The porphyrin-modified, p-GaInP<sub>2</sub> electrodes were run in a 3-electrode configuration with a platinum-mesh counter electrode and a SCE reference electrode. Each porphyrin-modified electrode was run in a variety of electrolytes. These electrolytes were a pH 4 phthalate buffer, a pH 7 phosphate buffer, a pH 10 carbonate buffer, all manufactured by Beckman Instruments. The p-GaInP<sub>2</sub> surfaces that were only etched and not treated with porphyrins are referred to as “untreated” surfaces.

Mott-Schottky analyses were run to determine the flat band potentials of the porphyrin-modified semiconductors. All Mott-Schottky analyses were run in the dark, using a Solartron SI 1287 Electrochemical Interface connected to a Solartron SI 1260 Impedance/Gain-Phase Analyzer. All data were collected using a scan rate of 20mV/sec and a frequency of 10KHz. Data collected in the dark usually had a potential window from -1.2 to +.2 V vs. SCE. The data were analyzed using a custom-built software program. Light analyses were also run to determine charge catalysis at the semiconductor/water interface. These consisted of multiple Mott-Schottky analyses run under a variety of light conditions. Additional testing included the application of various amounts of porphyrins to the surface of the semiconductor to determine whether this created a significant difference in band edge position.

## **Results**

The porphyrins were applied to the gallium indium phosphide surface by either drop-evaporation or running the 3-electrode cell in an aqueous porphyrin solution. For the porphyrins

that were applied by drop-evaporation, initial testing occurred in pH 7 phosphate buffer. The results of this testing are shown in Figure 1. Of the porphyrins studied, only three showed a statistically significant shift in the band edge position. These were TMpyPCl, NaTSPP, and CoTPP. CoTPP had a positive shift of 180mV in the flat band potential, so further studies were conducted on this molecule.

Again, CoTPP was applied by drop-evaporation. The test was performed in pH 4 phthalate buffer. The results of this test are shown in Figure 2. The band edges shifted in the positive direction by 400mV, past the water/oxygen redox potential.

A light analysis was performed on the CoTPP in pH4 buffer. The results of this testing are shown in Figure 3. Both the untreated electrode and the CoTPP-treated electrode show similar negative shifts in the flat band potential as the current density increases. In both electrodes, the charge transfer is not catalyzed.

Testing on CoTPP also included applying various amounts of the molecule to the Gallium Indium Phosphide surface. The application thickness is measured in terms of monolayers. The thickness of the application was determined from a study on similar porphyrins by Lamoen and Parrinello (1996) and Macor and Spiro (1983). Based on these estimates, a 10 monolayer application of CoTPP showed an additional 100mV shift in the band edge positions in pH 7 buffer. This analysis is shown in Figure 4.

## **Discussion and Conclusions**

Based on the results from the testing in pH 7 buffer as shown in Figure 1, NaTSPP, CoTPP and TMpyPCl were able to shift the band edges by a significant amount in the positive direction. The aim of these tests was to identify a molecule that would shift the band edges in a



positive direction past the water/oxygen redox potential. The results show that no porphyrin tested in pH 7 buffer was able to accomplish this. However, CoTPP was able to come within 110mV of the water/redox potential. Because of this, further study was performed on the CoTPP.

An additional finding from the testing of a variety of porphyrins was that the bandedge shifting characteristics of a porphyrin do not depend solely on the organic body of the molecule. Testing of FeTPPCL and CoTPPCL, which have the same organic structure, showed remarkably different bandedge shifting characteristics. While FeTPPCL shifted bandedges slightly in the negative direction, CoTPP shifted bandedges in the positive direction to 460mV. Based on this difference, it is apparent that the metal ion complexed at the center of the porphyrin plays a role in shifting band edges.

Testing in pH 4, shown in Figure 2, demonstrated remarkable results. At a lower pH, the water redox potential is shifted in a more positive direction. However, the bandedge shifting characteristics of the CoTPP are further enhanced in pH 4 buffer. Repeated testing on CoTPP showed a shift in the positive direction of 350mV, to 810mV. This moved the bandedges of the gallium indium phosphide electrode past the water redox potentials into an optimal water-splitting position. All of the tests up to this point were performed under dark conditions. What remained was to determine whether the CoTPP was able to maintain its bandedge-shifting characteristics under light conditions.

The results of this study are shown in Figure 3. Compared to an untreated electrode, the CoTPP is unable to sustain its bandedge shifting properties. The CoTPP is unable to catalyze the flow of the electrons from the gallium indium phosphide semiconductor to the water. This makes the electrons build up on the surface, shifting the bandedges in a negative direction as the

light intensity increases. As seen in the graph, there is very little difference between the charge catalyzing characteristics of an unmodified electrode and a CoTPP-modified electrode.

Final testing included varying the amount of porphyrin applied to the gallium indium phosphide. With a 0.1mM concentration of CoTPP and an area of  $105\text{\AA}$ , it was estimated that one 50 $\mu\text{L}$  drop will apply a .5 monolayer surface treatment on a  $.07\text{cm}^2$  gallium indium phosphide surface. As the application thickness increased to 10 monolayers, the bandedges shifted in a positive direction by 100mV. At a 15 monolayers thickness, the bandedges began shifting in the negative direction.

Our results show that CoTPP is the most successful bandedge-shifting molecule tested. Using pH4 phthalate buffer as an electrolyte can further enhance the bandedge shift by substantial amounts. This places the bandedges in an ideal water-splitting position. This can be further enhanced by applying a 10 monolayer coating of the CoTPP. Despite our initial hypothesis that a transition metal ion within a porphyrin would catalyze charge transfer, our results showed otherwise. At this stage of the research, we cannot determine with certainty why this is the case. However, our hypothesis is that the cobalt is unlikely to catalyze charge transfer because the cobalt is such a small part of the entire CoTPP molecule, and as such the cobalt will only come into contact with a fraction of the electrode surface. In addition, the bulky organic structure of the porphyrin is a poor conductor of electrons, as shown by Wrobel, Goc and Ion (1998). This characteristic of porphyrins further inhibits charge transfer.

If these hypotheses prove to be correct, a different approach must be found to shifting the band edges and catalyzing charge transfer. This approach may include the use of porphyrins. Research by Macor and Spiro (1983) has suggested that films of certain metalloprotoporphyrins with a thickness under 100 monolayers may be able to catalyze charge transfer. Further studies

by our group will look at these molecules to determine whether band edge modification and charge catalysis can occur.

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## Figures

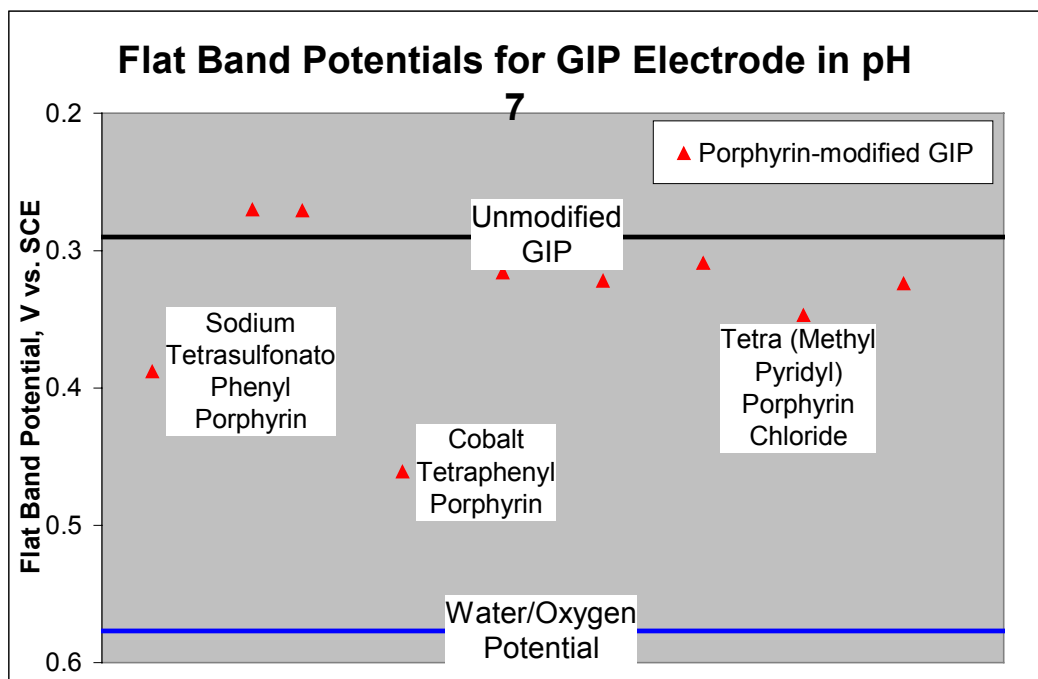


Figure 1. Shows the flat band potential of porphyrin-modified electrodes. Mott-Schottky analyses were performed to collect the data.

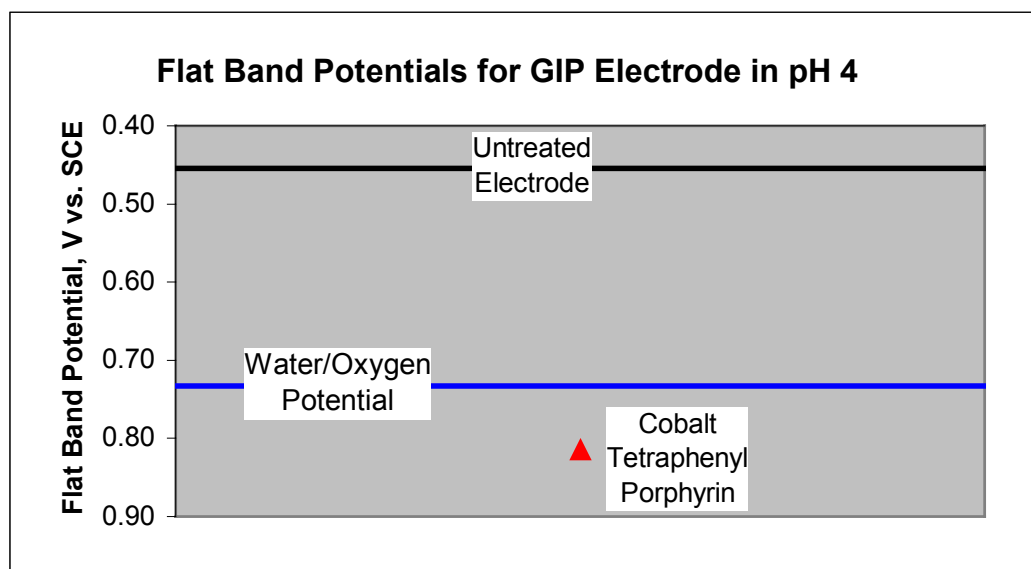


Figure 2. Shows the flat band potential of a CoTPP-modified electrode. The testing was performed in pH 4 buffer.

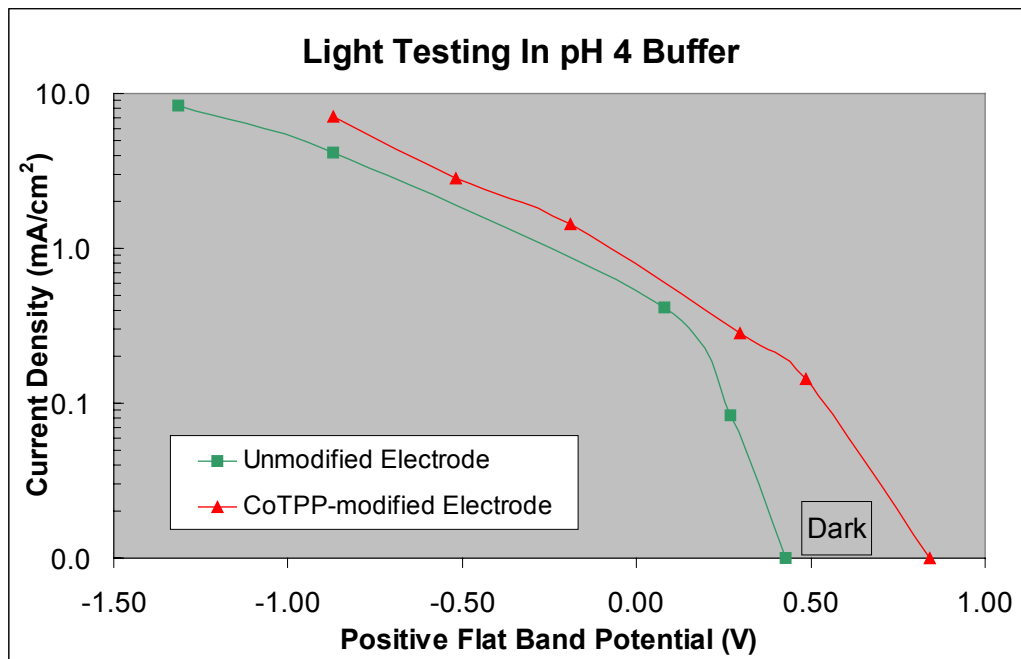


Figure 3. Light testing in pH 4 buffer. Charge transfer is not catalyzed by the CoTPP-modified electrode.

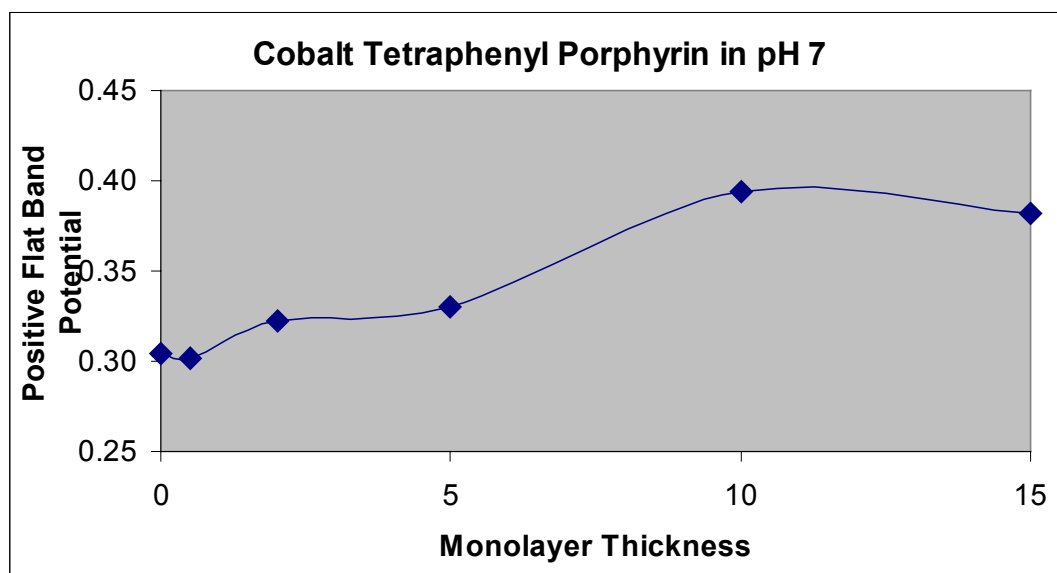


Figure 4. Shows how the band edges change with the increasing thickness of CoTPP application. Band edges shift an additional 100mV when the application thickness is increased from 1 to 10 monolayers.

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